

UDC 666.762.14:66.063.8.001.5

## FORMATION OF MULLITE OBTAINED BY COPRECIPITATION

N. M. Bobkova,<sup>1</sup> I. V. Kavrus,<sup>1</sup> E. V. Radion,<sup>1</sup> and N. F. Popovskaya<sup>1</sup>

Translated from *Steklo i Keramika*, No. 6, pp. 18 – 20, June, 1998.

The effect of the parameters of synthesis (precipitation pH, order of precipitation) of powders by coprecipitation in the  $Al_2O_3$  system is studied. The sequence of phase transformations in formation of mullite within the temperature range of 900 – 1400°C is investigated using structural analysis methods. The conditions of synthesis of experimental powders and heat treatment parameters facilitating maximum output of mullite are optimized.

Mullite-based ceramics generate significant interest owing to their properties: high refractoriness, relatively low coefficient of thermal linear expansion, high heat resistance, and increased chemical stability. This type of ceramic can be successfully used as high-temperature and friction material, in microcircuit substrates, protective coatings, etc. Moreover, mullite can be a component of composite materials, increasing their mechanical strength.

At present, in addition to the traditional solid-phase sintering, several new methods of mullite production that affect the sintering temperature of the finite product and its properties have been proposed. Powders for mullite synthesis are obtained by the sol-gel method, coprecipitation, thermal decomposition in spraying, and hydrothermal synthesis [1 – 3].

Solid-phase sintering at a temperature of 1600 – 1700°C produces sintered ceramics with a bending strength of 300 – 400 MPa, which is lower than in other construction materials, and yet this type of ceramic retains high strength up to 1000°C.

The sol-gel method makes it possible to control the particle size and ensures a high degree of component mixing, the possibility of increasing the strength of an article, and decreasing the sintering temperature [4]. However, this method involves using organometallic compounds, which are expensive and in short supply. The process also involves certain technological difficulties.

One of the most promising methods for obtaining high-quality ceramic materials is coprecipitation, the essence of which consists in joint precipitation from solutions of difficultly soluble precipitates with their subsequent washing, drying, and calcination. This method makes it possible to obtain finely dispersed precipitates (up to 0.05  $\mu m$ ), which significantly increases the rate of the solid-phase interaction and

decreases the sintering temperature. At the same time, the method provides for a high degree of mixture homogenization and increased purity [5]. The ceramic materials in these mixtures have improved and reproducible properties achieved at lower temperatures.

However, the list of publications dedicated to mullite synthesis by coprecipitation is rather limited. Moreover, most of them do not contain data on the sequence of technological processes and terms of their implementation. Significant discrepancies are observed in the final results and in the concept of the mechanism of mullite formation from synthesized precipitates in sintering (Japanese patent application 63-2806, USSR inventor's certificate 119345) [6, 7].

The materials used to obtain high-purity finely disperse mullite powder by coprecipitation included aqueous solutions of  $Al(NO_3)_3$ ,  $Al_2(SO_4)_3$ , and  $AlCl_3$  salts, aluminum acetate in combination with sodium alcoholate as a source of  $Al_2O_3$  and sodium silicate, Aerosil (silica powder), and colloidal silica as a source of  $SiO_2$ . The recommended pH of the solutions varies within a wide range and is probably determined both by the composition of the initial reagents and the sequence of their mixing. The aluminum hydrosilicate obtained as a precipitate is dried and sintered at temperature of 1150 – 1250°C, and sometimes 1400°C. It is noted that the mullitization process depends on the type of the initial materials [7].

These data are not sufficient for developing a clear technological procedure for mullite production by coprecipitation without additional research. That is why the present paper is dedicated to the study of the process of mullite formation by the coprecipitation method.

The initial reagents for synthesis of the crystalline phase of mullite were aqueous solutions of  $AlCl_3 \cdot 6H_2O$  and  $Na_2SiO_3 \cdot 9H_2O$  salts (1 M concentration). A 25% solution of ammonia was chosen as precipitator, since the use of solu-

<sup>1</sup> Belarusian State Technological University, Minsk, Belarus.

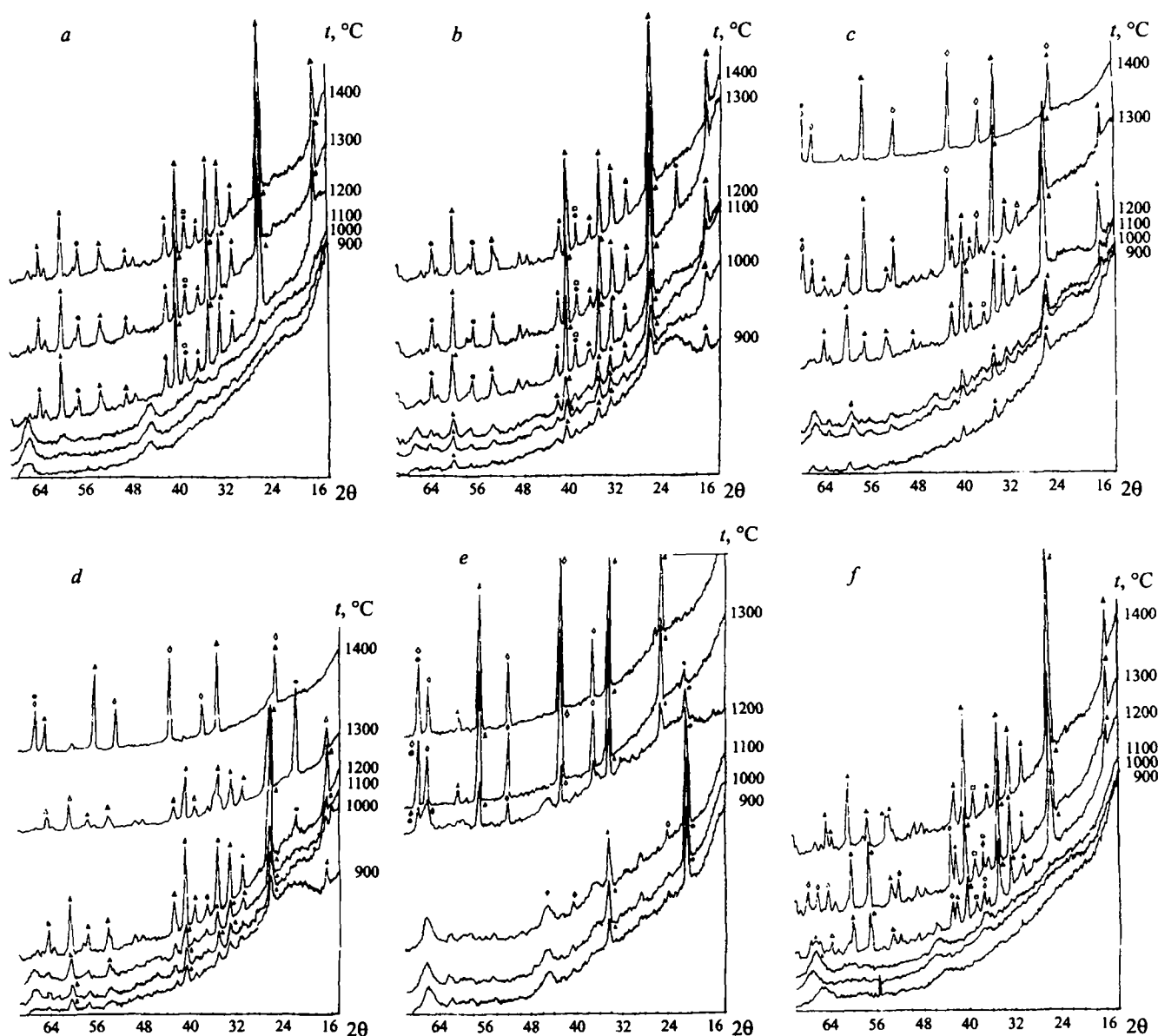


Fig. 1. X-ray patterns of precipitate cakes of compositions AS-6 (a), AS-9 (b), AS-7 (c), AS-10 (d), AS-8 (e), and AS-11 (f): ●) quartz, □)  $\text{Al}_2\text{O}_3$ , ◇)  $\text{Al}_2\text{O}_3$ , ▲) mullite, △) sillimanite.

tions of alkaline metal hydroxides results in contamination of the precipitates with cations.

The amount of reagents was calculated in order to obtain after complete precipitation a precipitate with a stoichiometric ratio of  $\text{Al}_2\text{O}_3 : \text{SiO}_2$  equal to 3 : 2, which corresponds to mullite. The salt : precipitator ratio was regulated by the specific values of the precipitation pH.

The sequence of precipitation is an important factor affecting the properties of hydroxide precipitate. Both direct and inverse precipitation were investigated. In direct precipitation, the precipitator was poured into the salt solution, in inverse precipitation, the solution of metal salts was poured into the precipitator solution. The rate of deposition of a precipitate has an effect on the dispersion. In our investigation, the solutions were poured together rapidly, since in this case the precipitate is more finely dispersed. Precipitation and ag-

ing of the precipitates (for 4 days) took place at room temperature. The terms of powder synthesis were varied by the pH value of precipitation and the order of precipitation (Table 1).

After ripening, the precipitates were filtered and repeatedly washed with distilled water to remove  $\text{Cl}^-$ ,  $\text{Na}^+$ , and  $\text{NH}_4^+$  cations. The precipitates obtained were dried in a drying cabinet at a temperature of 210–210°C to a constant mass and then pulverized. The experimental powders were subjected to high-temperature treatment at temperatures of 900–1400°C with a 100°C interval and 1-h holding at the maximum temperature.

In order to study the structure and phase composition, differential thermal, x-ray phase, and spectral analysis was carried out.

The DTA of the precipitate constituting the x-ray-amorphous product revealed the existence of two endothermic effects with maxima in the region of 145 – 160 and 294 – 340°C, reflecting the stepwise character of dehydration. An exothermic effect related to mullite crystallization was observed in the region of 930 – 1000°C. It was established from the DTA data that the calcination loss of the precipitate obtained by inverse precipitation is lower than that of the precipitate synthesized by direct precipitation. It should be noted that the precipitates obtained by direct precipitation contain a higher amount of thermally bound water.

The x-ray phase analysis of the heat-treated experimental powders showed that crystallization of the powders obtained by inverse precipitation of solutions starts at a temperature of 900°C, while the powders synthesized by direct decantation of the solutions are still x-ray-amorphous at this temperature.

In analyzing the x-ray phase curves of AS-6 and AS-9 compositions (Fig. 1a and b), it can be seen that the mullite phase in them is formed at temperatures of 900°C (AS-9) and 1100°C (AS-6). With a further increase in the temperature, the amount of mullite slowly increases. It can be inferred that at first, a structurally imperfect mullite appears, and then its crystal lattice is improved.

The x-ray patterns of AS-7 and AS-10 samples (Fig. 1c and d) indicate that formation of mullite proceeds via an intermediate crystalline phase, namely, sillimanite. The peaks corresponding to sillimanite are clearly visible up to the temperature of 1300°C, and in the x-ray patterns corresponding to 1400°C, these peaks are absent. Mullite peaks are clearly visible in the x-ray pattern. The AS-7 composition contains more sillimanite than the AS-10 composition. This is indicated by the fact that the AS-7 sample exhibits a higher number and intensity of sillimanite peaks.

In the x-ray patterns of the AS-8 sample (Fig. 1e) the transition of sillimanite to mullite is not clearly observed, while the AS-11 sample (Fig. 1f) exhibits a pronounced decrease in the intensity of the sillimanite peaks and an increase in the intensity of the mullite peaks in the temperature interval of 1300 – 1400°C.

The x-ray phase curves of the samples tested also exhibit some peaks of low intensity corresponding to various modifications of  $\text{Al}_2\text{O}_3$  ( $\alpha$ ,  $\gamma$ ) and  $\text{SiO}_2$  (quartz).

Since the interplanar distances and the peak intensities of mullite and sillimanite are close to each other, the infrared spectra of the samples were taken in order to determine more accurately the composition of the emerging phases.

The infrared spectra of the AS-6 and AS-9 samples support the data from the x-ray phase analysis of these compositions. The IR spectra exhibit mullite peaks at the temperature of 900°C, and they become clearer with an increase in the temperature. At the same time, other samples at the tempera-

TABLE 1

Composition	Terms of precipitation	
	pH	precipitation order
AS-6	6	Direct
AS-7	7	The same
AS-8	8	The same
AS-9	6	Inverse
AS-10	7	The same
AS-11	8	The same

ture of 1200°C distinctly exhibit sillimanite peaks which become less distinct at 1300°C and disappear completely at 1400°C. For mullite, the opposite tendency is observed: with an increase in the temperature, the mullite peaks become clearer.

As a result of the investigations carried out, it was established that at pH = 6, formation of mullite starts at the temperature of 900°C. In the case of the inverse order of precipitation, this process proceeds more intensely. With an increase in the pH to 7 – 8, synthesis of mullite proceeds via a transitional phase, namely, sillimanite, which agrees with the new version of the phase diagram of the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system published by A. S. Berezhnoi [8].

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